Proceedings of the American Academy of Arts and Sciences.

Vol. XLV. No. 9. — March, 1910.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

NOTES ON CERTAIN THERMAL PROPERTIES OF STEAM.

By Harvey N. Davis.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

NOTES ON CERTAIN THERMAL PROPERTIES OF STEAM.

By Harvey N. Davis.

Presented by John Trowbridge, December 8, 1909; Received December 30, 1909.

§ 1. Introduction 267
§ 2. On the C_p values available for the present purpose 269
§ 3. On the total heat of saturated steam
A. The determination of $H - H_{100}$ 272
B. The value of H_{100} 280
C. Extrapolation formulæ for H and L 281
§ 4. Discussion of the specific heat of superheated steam, including
A recomputation of Regnault's values 285
Computations based on the Joule-Thomson effect 289
Computations with Planck's equation 295
§ 5. Clausius' "Specific heat of saturated steam" 303
§ 6. The critical volume of water 305
Summary of the results in this paper 310

1. Introduction.

It is the purpose of this paper to collect and correlate certain material on the thermal properties of steam. A part of this material was published in a technical journal a year ago.[1] Other parts of it have been contributed as discussion of papers by others in that journal and elsewhere. Still other parts of it have been used in a recent book.[2] The rest appears here for the first time. It all centers around a new determination of the total heat of saturated steam.

The previous determinations of the total heat of steam (H), and of the closely related latent heat of evaporation (L), will first be summarized. The most famous of them was published by Regnault in 1847. His experiments were so numerous, covered such a wide temperature range, and were characterized by such perfection of detail as to be accepted as the foundation of the engineering practise of the world,

[1] Jour. Am. Soc. of Mech. Engs., 1908, **30**, 1419.
[2] Marks and Davis, Steam Tables and Diagrams.

and to remain standard for sixty years. He himself deduced from them the well-known linear formula

$$H = 606.5 + 0.305\ t \text{ calories.}$$

Others have represented them by second degree formulæ with negative second degree terms.

The more modern experimental work began in 1889 with a measurement of L at 0° C. by Dieterici.[3] He was followed by Griffiths,[4] Joly[5] and Smith,[6] working at various temperatures between 0° and 100° C., and finally in 1906 by Henning,[7] of the Reichsanstalt, who published an excellent series of values covering the range from 30° to 100° C. The results of all these observers are in excellent agreement and show that Regnault's formula for H gives values which are much too high near 0° and somewhat too low near 100°.

In 1908 the formula which is the basis of this paper was presented to the American Physical Society[8] and to the American Society of Mechanical Engineers.[9] It was based on the results of certain throttling experiments by Grindley,[10] Griessmann[11] and Peake.[12] These experiments were originally undertaken for the purpose of computing, with the help of Regnault's total heats, the variation with pressure and temperature of the specific heat, C_p, of superheated steam. This attempt was unsuccessful, because the total heats entered into the computations in such a way as to cause the errors in them to be tremendously magnified in the results. The desired information about C_p has since been obtained in other more direct ways, and the throttling experiments have been ignored. It is, however, possible, by reversing the computation processes of Grindley, Griessmann and Peake, to proceed from the recently determined values of C_p which were to have been their goal, back to a new determination of the values of H which were their starting point. The very sensitiveness of their procedure to errors in H ensures the insensitiveness of the

---

[3] Wied. Ann., 1889, **37**, 494.
[4] Phil. Trans., 1895, **186** A, 261.
[5] In an appendix to Griffiths' paper, page 322.
[6] Phys. Rev., 1907, **25**, 145.
[7] Wied. Ann., 1906, **21**, 849.
[8] Phys. Rev., 1908, **26**, 407.
[9] Journal, loc. cit.
[10] Phil. Trans., 1900, **194** A, 1.
[11] Zeit. Ver. d. Ing., 1903, **47**, 1852, and 1880; also Forschungsarb., 1904, **13**, 1.
[12] Proc. Roy. Soc., 1905, **76** A, 185.

present procedure to errors in C_p. The result of such a reversal of their reasoning is the formula which was suggested two years ago, namely,

$$H = H_{100} + 0.3745\ (t - 100) - 0.000990\ (t - 100)^2.$$

This formula belongs only to the range between 100° and 190° C. Within this range its accuracy is believed to be of the order of one tenth of one per cent.

When the new formula was announced, there were no direct experimental determinations of H or L above 100° by which it could be checked except Regnault's, but more recently Henning [13] has published a continuation of his admirable research to 180°. The extent of the agreement of this with the formula will be discussed later.

As has been indicated, the computations leading to the new formula involve two different sorts of experimental data. The first of these, namely, the throttling experiments of Grindley, Griessmann and Peake, have been sufficiently discussed in a previous paper.[14] The second, the direct determinations of C_p mentioned above, will be discussed in the next section.

2. On the C_p Values Available for the Present Purpose.

There are three direct calorimetric determinations of the variation of C_p with pressure and temperature, namely, those of Lorenz,[15] of Knoblauch and Jakob [16] and of Thomas.[17] That of Lorenz was the earliest of the three and was, as he himself says, a preliminary survey for the sake of those engineers who could not afford to wait for more accurate work. It is not ordinarily considered comparable with Knoblauch's.

Both Knoblauch's and Thomas' results were obtained by determining the electrical energy necessary to increase by a known amount the temperature of previously superheated steam. In Knoblauch's apparatus the original superheating took place in an electrical preheater. The steam was then still further heated in a separate calorimeter, the energy added being the object of a direct measurement. In Thomas' case the separate preheating and calorimetric coils of Knoblauch's apparatus were replaced by a single coil, by means of which initially wet steam was brought, first just to dryness, and in a later experiment

---

[13] Wied. Ann., 1909, **29**, 441.

[14] These Proceedings, page 241.

[15] Zeitsch. Ver. d. Ing., 1904, **48**, 698; Phys. Zeitsch., 1904, **5**, 383; and Forschungsarb., 1905, **21**, 93.

[16] Zeitsch. Ver. d. Ing., 1907, **51**, 81 and 124; Forschungsarb., 1906, **35**, 109.

[17] Proc. Am. Soc. Mech. Engs., 1907, **29**, 633.

to a high superheat. The amount of energy necessary for the superheating was then found by a subtraction. It is, therefore, liable to a percentage error much greater than that in either of the observed components. Knoblauch's method is obviously preferable to Thomas' in this respect.

His experimental arrangements also seem superior to Thomas'. In his separate calorimeter there were only small temperature differences between the inlet and outlet pipes; in Thomas' combination calorimeter there were very large differences. In Knoblauch's case the heat losses through these pipes were determined; in Thomas' case they

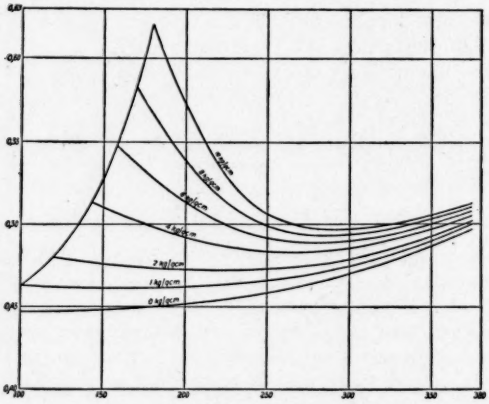

FIGURE 1. Knoblauch's Cp. diagram.

were ignored. Furthermore, although both calorimeters were very carefully lagged, Knoblauch determined his radiation losses in each experiment, while Thomas, in the final form of his apparatus, relied on eliminating them, a difficult thing to be sure of. Finally, Knoblauch's thermometry is apparently more refined than Thomas'. It is therefore probable that wherever the two sets of results disagree, Knoblauch's are to be preferred.

As a matter of fact, the two sets of results agree fairly well in the region of moderate superheats, as will be seen in Figures 1 and 2, but disagree fundamentally in exactly that part of the diagram which will be most used in what follows, namely, the region of moderate pressures and very low superheats (the lower left-hand corner of Figure 1). The

sudden rise in Thomas' curves near saturation indicates, according to his interpretation, that a comparatively large amount of heat is required to change dry steam into slightly superheated steam. But it may also indicate that what he believed to be dry steam really carried a small amount of water floating as a mist. This would have to be evaporated at the expense of some extra heat in addition to that required for the actual superheating, and C_p would come out too large.

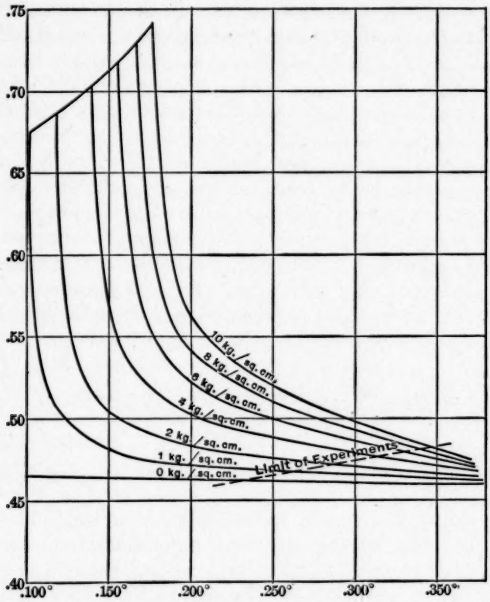

FIGURE 2.

That this explanation is a reasonable one is shown by a comparison of his apparatus with Knoblauch's. The latter's preheater, mentioned above, was a pipe made up of 15 sections each 20 cms. in diameter and 20 cms. long, each filled with a dense grid of constantan ribbons which ensured thorough mixing of the passing steam. All of the heat necessary for the desired superheating was ordinarily put in in the first one or two sections, and the sole purpose of the rest of the preheater was to bring the resulting mixture of highly superheated steam and floating

mist into a homogeneous state. Knoblauch and Jakob say that traces of moisture were observable through several of the mixing sections, and it is easy to show that even if "several" means as few as two, and even if the steam in these sections had always had the greatest specific volume which it ever had, the floating mist must have persisted for a time which was never less than a second and averaged more than two seconds, and this after *all* of the heat necessary for the high superheat had been put in. In Thomas' apparatus, on the other hand, the evaporation and superheating had to take place in 24 quarter-inch holes in a soapstone block something like 5 inches long, and in a small chamber just above it, and a similar computation shows that even if the specific volume of the steam had never been greater than that of the original saturated steam, it must have passed the thermocouple, always within nine tenths of a second, sometimes within a thirtieth of a second, and on the average within less than half a second of the time when the *first* of the superheating heat was put in. It is, therefore, very probable that Thomas' "saturated steam" was slightly wet, and that the percentage of moisture passing the thermocouple decreased from experiment to experiment as the final superheat was increased, giving too high values of C_p near saturation. Knoblauch's values have therefore been used in preference to Thomas' in this work. Confirmations of this decision will be found on pages 287, 298 and 302.

3. The Total Heat of Saturated Steam.

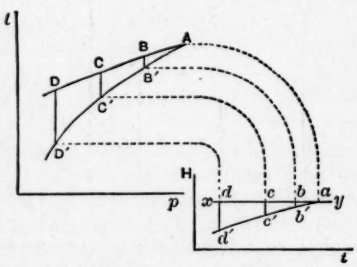

Fig. 3. Fig. 4.

Showing how the Total Heat Curve $ab'c'd'$ is obtained from a Throttling Curve ABCD.

A. *The determination of* $H - H_{100}$. — A part of the following account of the method by which the total heat of saturated steam has been computed is reprinted with minor changes from the Proceedings of the American Society of Mechanical Engineers.

Let Figure 3 represent a throttling curve of the sort published by Grindley, Griessman or Peake. Supposedly dry and saturated steam at the pressure and temperature corresponding to the point A is first throttled to lower pressure and temperature corresponding to the point B; then in a later experiment

in the same run, it is throttled from exactly the same initial condition A to the condition C; then to D and so on. The well-known law of throttling is that the total heat in the condition B, or C, or D, is equal to that in the initial condition A.

The point B represents superheated steam at the pressure p_B; the point B′ represents saturated steam at the same pressure; and the amount of superheat at B is the measured temperature there minus the temperature at B′, which can be taken from a steam table. Also, by definition, the total heat at B equals that of saturated steam at the same pressure (point B′) plus the amount of heat required to superheat it at constant pressure from B′ to B. This is the integral of C_p from B′ to B, or simply the mean C_p from saturation multiplied by the known superheat. If C_p is known, this integral, or increment in the total heat between B′ and B, is easily evaluated.

This integral is not only the difference between the total heat of saturated steam at B′ and that of superheated steam at B; it is also the difference between the total heat of saturated steam at B′ and that of saturated steam at A; that is, between the two corresponding ordinates of the curve that gives the total heat of saturated steam as a function of the temperature, the curve sought in this paper. To draw a piece of this curve, one chooses arbitrarily some horizontal line such as *xy* in Figure 4, and lays off below it, at the proper temperatures, the distances bb', cc', dd', etc., which represent on the desired H-scale the integrals or total heat differences between B′ and B, C′ and C, D′ and D, etc. The curve $ab'c'd'$ is an isolated piece of the true curve of total heat against temperature. The *relative* height of its points, that is, its shape, is accurately determined; the *absolute* height above the usual zero of total heats, namely, that of water at 0°C., is as yet wholly unknown. The experiments of Grindley gave seven independent sample pieces of this sort, one for each throttling curve, their temperature ranges being known and greatly overlapping; similarly Griessmann's data gave eleven such sample pieces, and Peake's six.

As was explained in the preceding paper on the Joule-Thomson effect, Grindley's incoming steam (point A), and occasionally Peake's, was not quite dry, so that its total heat was not determined by its pressure and temperature. Whenever this seemed to be the case, the points A and *a* of Figures 3 and 4 were left out of consideration altogether. BCD would still be a curve of constant total heat, provided only that the quality of the incoming steam at A remained constant during a run, and $b'c'd'$ would still be a useful piece of the desired total heat curve.

All sample pieces of any one observer were then plotted carefully on

very thin transparent rice paper, with vertical guide-lines at certain standard temperatures, which enabled these plots to be accurately oriented as far as rotation and horizontal displacement were concerned, but left them free to slide up and down over each other. The sheets were then piled on top of one another on a transparent table lighted from below, each one placed so as to make its piece of curve coincide most satisfactorily with the overlapping pieces already laid down. The exact relative displacements of the sheets were then carefully measured. This process was repeated for each of the three observers' sets of sheets independently, four different times for each set, in two very different orders and in those orders reversed, on different days, all with the object of avoiding as far as possible any routinizing effects of memory or habit which might disturb the real independence of the four determinations. The means of the measured displacements were then used to reduce each of the pieces of curve in any one of the sets to a zero common to all the curves of that set. The results are marked *Gy*, *Gs*, and *P* in Figure 5. They are plotted separately for clearness, but they are simply different experimental determinations of exactly the same real curve. The vertical scale of each is that indicated at the side of the diagram, but the height of each above its true zero is still unknown. Each of the circles represents at least one independent throttling observation, and some of them two or three independent observations that happened to coincide. It will be noticed that no one of the curves is more than a fifth of a scale division, or four tenths of a calorie, wide between centers. Each is, therefore, a self-consistent determination of the true curve within two tenths of a calorie, or about three hundredths of one per cent.

The next step was to establish a comparison between the three curves. The points of each were first divided into groups, each including some 20° of temperature range, and the mean point of each group was used to represent the group. This procedure is justified by the fact that so short a section of the total heat curve can be considered straight without serious error. There were eighteen such means, seven representing Grindley's points, five Griessmann's and six Peake's. These means were then plotted on three more sheets of rice paper, the resulting curves were superposed in the way already described, and a determination was made of the corrections necessary to reduce all three sets of means to a common but still arbitrary zero.

In the meantime successive means from each of the three curves taken separately were used to compute the values of the derivative dH/dt which are plotted with large circles in Figure 6. It is evident that the results from the three sources agree with each other in deter-

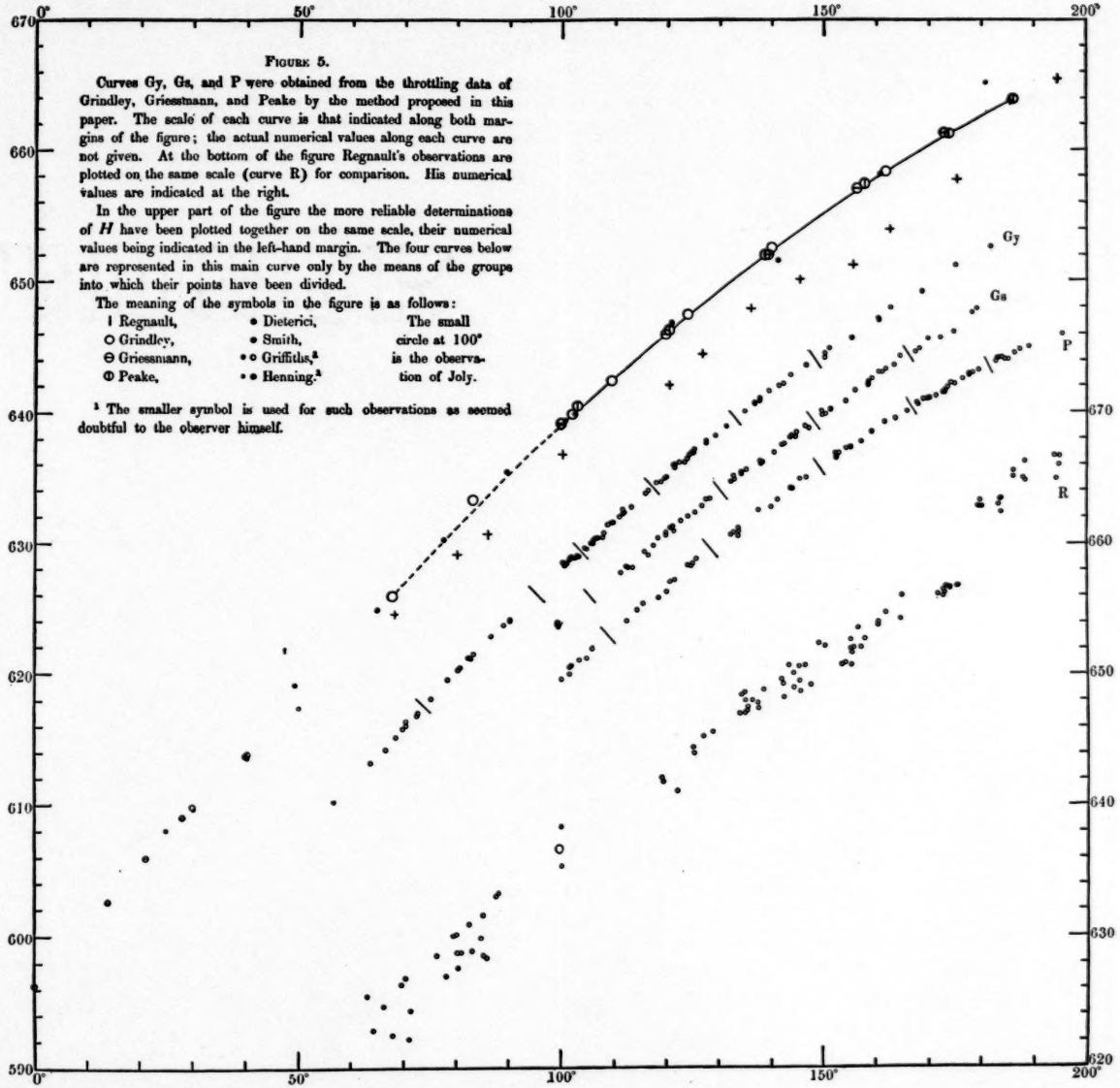

FIGURE 5.

Curves Gy, Gs, and P were obtained from the throttling data of Grindley, Griessmann, and Peake by the method proposed in this paper. The scale of each curve is that indicated along both margins of the figure; the actual numerical values along each curve are not given. At the bottom of the figure Regnault's observations are plotted on the same scale (curve R) for comparison. His numerical values are indicated at the right.

In the upper part of the figure the more reliable determinations of H have been plotted together on the same scale, their numerical values being indicated in the left-hand margin. The four curves below are represented in this main curve only by the means of the groups into which their points have been divided.

The meaning of the symbols in the figure is as follows:

| Regnault,	• Dieterici,	The small
○ Grindley,	• Smith,	circle at 100°
⊖ Griessmann,	•○ Griffiths,[1]	is the observa-
⊕ Peake,	•• Henning.[1]	tion of Joly.

[1] The smaller symbol is used for such observations as seemed doubtful to the observer himself.

mining a straight line as the graph of dH/dt against t. The total heat curve itself can therefore be represented in the range between 100° and 190° by an equation of the second degree in t, within the limit of error of the available data. The form selected is

$$H = H_{100} + a\,(t - 100) - b\,(t - 100)^2.$$

The eighteen means, reduced to a common but still arbitrary zero, were

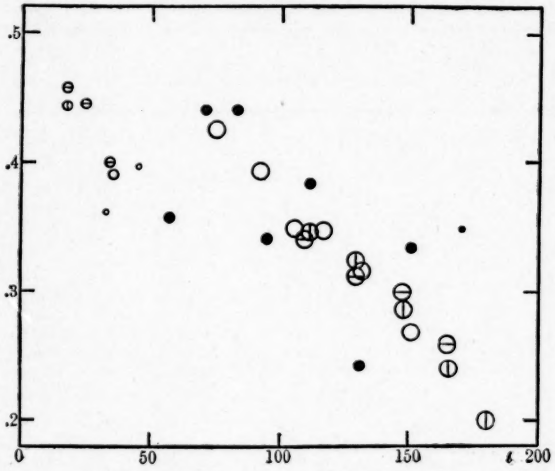

FIGURE 6. dH/dt plotted against t. The symbols refer to the same authorities as in Figure 5.

used to give a least squares determination of the constants H_{100}, a and b and of their probable errors, with the following results;

$$\begin{aligned} H_{100} &= \text{arbitrary} \pm 0.03, \\ a &= 0.3745 \pm 0.0014, \\ b &= 0.000990 \pm 0.000020. \end{aligned}$$

The agreement of the eighteen individual means with this formula is shown in the upper part of Figure 5, the curve being drawn to represent the formula as accurately as possible. It is also shown by the smallness of the three probable errors. Even if these errors are combined in the most unfavorable way, the change in the computed value of H at 200°C. is only 0.37 calories, or about one eighteenth of one per cent of H itself; at lower temperatures the change would be still less.

The value of H_{100} which was obtained from the least squares process is entered in the above table as "arbitrary" because it is measured from an arbitrary zero. This value of H_{100} was next subtracted from each of the eighteen means, giving new values for these means on a new scale whose zero is H_{100}. In other words, these means now represent the true values of $H - H_{100}$. The resulting values are given in Table I, and are represented within their limit of error by the formula

$$H - H_{100} = 0.3745\ (t - 100) - 0.000990\ (t - 100)^2.$$

TABLE I.

VALUES OF $H_t - H_{100}$ AND OF H_t.

	t	$H_t - H_{100}$	H_t*
Grindley	67.56	−13.23	625.88
	82.70	− 6.80	632.31
	101.80	+ 0.71	639.82
	109.27	+ 3.31	642.42
	123.82	+ 8.36	647.47
	139.92	+13.46	652.57
	161.55	+19.26	658.37
Griessmann . . .	99.61	+ 0.03	639.14
	119.80	+ 6.89	646.00
	139.18	+12.94	652.05
	156.01	+17.98	657.09
	172.60	+22.28	661.39
Peake	102.88	+ 1.15	640.26
	120.22	+ 7.16	646.27
	138.41	+12.87	651.98
	157.56	+18.36	657.47
	173.60	+22.22	661.33
	186.33	+24.77	663.88

* These values of H_t are computed from $H_t - H_{100}$ on the assumption that H_{100} = 639.11 mean calories (see page 281). They are inserted here for the convenience of the reader, but the values of $H_t - H_{100}$ are the significant part of this table and indeed of the whole paper.

This formula gives, in mean calories, the total heat of saturated steam at any temperature between 100° and 190° C. *in terms of that at* 100° C. A value for the fundamental constant H_{100} will presently be chosen from those available in the literature of the subject, but it should be remembered that even if this choice is wrong, or if new and different data near 100° are hereafter published, whatever merit the above equa-

tion may have will be wholly unaffected by the necessary change in H_{100}.

It is interesting to compare the self-consistency of this work, as represented by the narrowness of the bands of plotted points, with that of Regnault's observations, which are plotted at the bottom of Figure 5.[18] His band is at least eight or ten times as wide as any of

TABLE II.

HENNING'S MEASUREMENTS OF H.

Temp.	Value of L.		Heat of the liquid.	H.	H_{100}-H.	H_{100}.	Variation from	
	As reported.	Reduced.					First mean.	Second mean.
30.12	(579.0)	(579.5)	30.1	(609.6)	....	....	....	....
49.14	569.55	570.07	49.09	619.16	....	....	....	....
64.85	559.47	559.98	64.77	624.75	+14.39	639.14	−0.19	−0.12
77.34	552.47	552.97	77.27	630.24	+ 8.99	639.23	−0.10	−0.03
89.29	545.76	546.26	89.24	635.50	+ 4.13	639.63	+0.30	+0.37
100.59	538.25	538.74	100.59	639.33	− 0.22	639.11	−0.22	−0.15
102.34	536.93	537.42	102.35	639.77	− 0.87	638.90	−0.43	−0.36
120.78	525.32	525.90	121.02	646.92	− 7.36	639.56	+0.23	+0.30
140.97	509.60	510.06	141.62	651.68	−13.79	637.89	−1.44	....
160.56	495.95	496.40	161.80	658.20	−19.06	639.14	−0.19	....
180.72	481.99	482.43	182.78	665.21	−23.79	641.42	+2.09	....
				Mean of all		639.33	±0.49	....
				Mean of first six		639.26	....	±0.19

The values of L in the second column are in terms of Henning's "15° Calorie" of 4.188 international Joules; those in the third column are reduced to mean calories of 4.1842 Joules. The heat of the liquid in the fourth column is from the steam tables of Marks and Davis. The probable error of each mean is 0.845 times the corresponding average error.

those above it. It should also be noticed that something evidently happened to his apparatus at 178° C., and that allowing for this, his band shows unmistakably the same curvature as those above it. The observations above 178° C. were, as a matter of fact, the last he made, and he speaks definitely of serious trouble with his apparatus at the

[18] The large circle at the boiling point, 100° C., represents the mean of 38 points, of which only the highest and lowest are plotted.

very point at which the jump occurs; in fact, he had to renew many of its parts, and to watch it continually thereafter, so that his conditions may well have been somewhat changed. This discontinuity in his curve has been noticed by many writers, one of whom attributes it to a leak in his distributing valve, remedied at this point; but this is not definitely mentioned in the memoir.

The recent publication by Henning of his measurements of L between 100° and 180° gives a valuable test of the new formula. All his values in both papers are collected in the second column of Table II. They are expressed in terms of a calorie of 4.188 [19] international Wattseconds. It is probable that the mean calorie (0° to 100°) is about 4.184(2) international Wattseconds, for the fine work of Reynolds and Moorby [20] by a mechanical method, leads, according to Smith, [21] to the value 4.1836, while the equally good work of Barnes [22] by an electrical method must now [23] be regarded as leading to the value 4.1849. Each of Henning's numbers should therefore be multiplied by 4.188 / 4.1842 = 1.00091. The results are given in the third column of Table II. They lead to the values of H in the fifth column. In the sixth and seventh columns are given the values at the corresponding temperatures of

$$H - H_{100} = 0.3745\ (t - 100) - 0.000990\ (t - 100)^2.$$

and of H_{100} itself. The latter is practically constant as it should be if the new formula is true. It will be noticed that the probable error of the mean value of H is only one thirteenth of one per cent of that mean, and that this agreement is within the one tenth of one per cent which Henning claims for his observations. It will further be noticed that practically all of the discrepancy is in two of the last three values. If all three of these values are omitted, so that the range of the test is cut down to that between 65° and 121°, the probable error of the new mean is only ± 0.19 calories, or one thirty-fourth of one per cent.

In estimating the significance of the comparatively great disagreement between Henning's value at 180° and the new formula it should be remembered that Henning himself says, "Bei der höchsten Temperatur von 180° konnten nur an zwei tagen Versuchen angestellt werden" (instead of on four days as at most of the other temperatures).

---

[19] This is Jäger and von Steinwehr's value for the 15° calorie. The justification for it has not yet been published.

[20] Phil. Trans., 1897, **190** A, 301.

[21] Monthly Weather Review, 1907, **35**, 458.

[22] Phil. Trans., 1902, **199** A, 149.

[23] Proc. Roy. Soc., 1909, **82** A, 390.

"Zu Beginn des dritten Tages versagte der Apparat seinen Dienst und es war infolge der durch die starke Hitze eintretenden allmählichen Veränderungen des Materials und inbesondere infolge der Abnutzung des Hahnes H nicht wieder der erforderliche Grad der Dichtheit zu erreichen." If a small leak of the same sort had been present without being noticed on the two days on which observations were made, its effect would have been to make the observed L too large, just as it seems to be. At any rate, the point at 180° is not entitled to nearly as much weight as the others. The point at 140° was, however, as far as Henning could judge, as good as any of the rest.

One other aspect of Henning's paper tends to minimize the significance of the disagreement at the two high temperatures. He is led by his points at 140° and 180° to the conclusion that the curve $L = f(t)$ is a straight line between 120° and 180°. Now, of course, it is possible that he and Regnault are both right in finding unexpectedly high values near 180°, and that, because of changing polymerization or some other disturbing condition, the character of the curve $L = f(t)$ between 120° and 180° is very different from that which it is known to have below 120° and from that which it must begin again to have somewhere above 180°, if it is to come vertically to zero at the critical temperature as is commonly supposed. This is, however, not probable, and until Henning's 180° point is definitely verified by observations with unquestionable apparatus, the writer will still believe that the formula proposed in this paper is nearer the truth than is Henning's straight line. The excellence of the confirmation between 65° and 121° and also at 160° seems more significant than the disagreements at 140° and 180°.

Another check of the new H formula can be obtained by computing from it the specific volume of saturated steam by means of Clapyron's equation

$$v = v' + J \frac{L}{T} \frac{1}{(dp/dv)_{\text{sat.}}}.$$

This check has been carried through independently by Peabody[24] and by the writer.[25] In both cases the necessary values of dp/dt were taken from the recent paper of Holborn and Henning on the saturation pressures of steam,[26] and the values of L were based on the formula proposed in this paper. The choice of a suitable value for H_{100} and of suitable values for the heat of the liquid which has to be subtracted

[24] Proc. Am. Soc. Mech. Engs., 1909, **31**, 595.
[25] Marks and Davis, Steam Tables.
[26] Wied. Ann., 1908, **26**, 833.

from H to give L, was in each case accomplished independently of, and to a minor extent in disagreement with, the judgment of the other, but in each case the greatest difference between the computed values and those actually observed by Knoblauch, Linde, and Klebe[27] was under two tenths of one per cent, and in each case the average of the deviations was about one tenth of one per cent and they were nearly equally divided between plus and minus. It is probable that some of these deviations may properly be attributed to errors in the observed values.

The accuracy of the new H formula can now be estimated. It has been pointed out that the self-consistency of the computed points indicates a precision of the order of a twentieth of one per cent. The actual error is probably larger than this because of systematic errors in Knoblauch's specific heats. It is possible that these will ultimately be raised enough to make H_{190} a tenth or even a sixth of one per cent larger. Inasmuch, however, as the other two tests which have been applied, based on Henning's direct measurements of H and on Knoblauch, Linde, and Klebe's volume measurements, have both led to an estimated accuracy of a tenth of one per cent or better, a part of the outstanding disagreement in each case being furthermore reasonably attributable to possible errors on the observed as well as on the computed side of the comparison, it would seem that a claim of a tenth of one per cent for the accuracy of the new H formula between 100° and 190° is justified.

B. *The value of* H_{100}. — In what is to follow a suitable value for H_{100} will be necessary. Henning's work has already been shown to lead to the value

$$H_{100} = 639.26 \text{ mean calories (Henning).}$$

Another available value is that of Joly[28] who compared the latent heat of steam at 99.96° with the mean specific heat of water between 11.89° and 99.96°. The latter number is 0.99949 according to the curve used in the steam tables already mentioned. The resulting value of H_{100} is

$$H_{100} = 638.82 \text{ mean calories (Joly).}$$

In this determination of H_{100} Regnault's measurements will not be considered at all. They show unmistakable evidence of running lower than they should, probably for the same reason that makes

[27] Forschungsarb., 1905, **21**, 33.
[28] *Loc. cit.*, on page 268.

Thomas' values of C_p at saturation correspondingly too high. Only recently has it become evident how difficult it is to remove the last traces of moisture from apparently dry steam, and if any remained in Regnault's steam, it would have made his results too low, just as they seem to be.

The mean of Henning's and Joly's values of H_{100} is 639.04 if both are weighted alike, or 639.11 if Henning's has (as it seems to deserve) twice the weight of Joly's. The final formula for H is, therefore,

$$H = 639.11 + 0.3745\ (t - 100) - 0.000990\ (t - 100)^2 \text{ mean calories.}$$

The steam table of Marks and Davis, which was computed before the appearance either of Henning's second paper or of Barnes' revision of his value of J, was based on $H_{100} = 639.08$, which, as it happens, is between the two means just found, and nearer to either of them than the limit of error of the work demands. The values of H, L and L/T in that table will be used in the rest of this paper as representing the best available data.

C. *Extrapolation formulæ for H and L.* — The range within which the new H formula holds has been set as from 100° to 190°. Above the latter temperature no observations are available. It is often important, however, both in scientific and in technical work, to have at least reasonably accurate steam tables at considerably higher temperatures. It is, therefore, desirable to develop as safe an extrapolation formula as possible for either H or L.

For this purpose the second degree H formula proposed above is wholly unsuited. Within the range for which it is proposed, it happens to be an unusually good three term Taylor's series development of the true function but it cannot be extrapolated safely either up or down.

That it cannot be used near 0°, is seen from Figure 6, where the small circles, not previously mentioned, represent values of the derivative of H with respect to t, obtained from the five sets of experimental values mentioned on page 268. It is evident that the graph of dH/dt against t is not a straight line over the whole range from 0° to 200°. No second degree formula that fitted the observations above 100° could be expected to reproduce those near 0° also.

That a second degree formula is no less unsatisfactory for a extrapolation to high temperatures can be shown as follows. Let it be assumed that the top of the steam dome on either the $p\ v$ or the T N (temperature-entropy) plane is round like Figure 7*a* and not pointed like Figure 7*b*.[29] This is the usual assumption, and it is corroborated

[29] It follows from the Clapyron equation that if the dome is round on either plane, it will be on both.

by the work of a number of observers.[30] Now according to a familiar equation of thermodynamics

$$dH = T\,dN + v\,dp$$

for any transformation, and in particular for one along the saturation line. Dividing by dt and passing along that line to the critical temperature as a limit, gives

$$\lim_{T \doteq T_c}\left(\frac{dH}{dt}\right) = T_c \lim_{T \doteq T_c}\left(\frac{dN}{dt}\right) + v_c\left(\frac{dp}{dt}\right)_{\text{sat. crit.}}$$
$$= -\infty \qquad + \text{constant.}$$

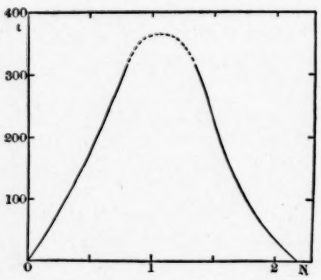

FIGURE 7 *a*.

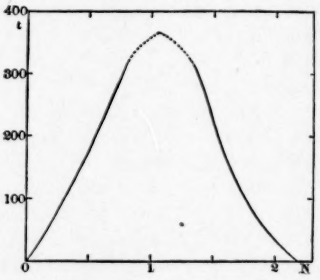

FIGURE 7 *b*.

The steam dome on the temperature-entropy plane. The full lines are drawn to scale; the dotted lines show two possible shapes near the critical point, of which the first is almost certainly right.

That is, H must not only pass a maximum below the critical temperature, but must approach that temperature with so sharp a turn downward as to reach it with a vertical tangent. The H curve is throughout a curve not only of constantly changing slope but also of constantly increasing curvature as is shown in the upper part of Figure 8, and it is only in very limited regions that the first three terms of a Taylor's development can be expected to represent it with sufficient exactness. It might be possible to invent a function having the general properties indicated by Figure 8, if one knew the value of H at the critical

[30] See for example papers by Cailletet and Mathias, C. R., 1886, **102**, 1202, and 1887, **104**, 1563; by Amagat, C. R., 1892, **114**, 1093; and by Young, Phil. Mag., 1900, **50**, 291. See also the diagrams for normal pentane on pages 166 and 167 of Young's book on Stoichiometry, Longman's (1908).

temperature. Inasmuch as nothing is known about that final value of $H_{sat.}$, such an empirical treatment gives no promise of significance.

In the case of L, on the other hand, one learns from an inspection of figure 8, not only that $dL/dt = -\infty$ at the critical point, but also that $L = 0$ there. This led Thiesen in 1897,[31] to the fortunate suggestion

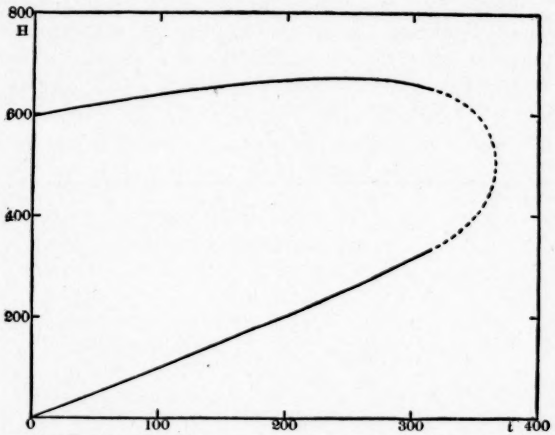

FIGURE 8. The steam dome on the Ht plane, showing the relationship between the graphs representing the "total heat of saturated steam" and the "heat of the liquid." The former (the upper boundary of the steam dome) is the curve that Regnault believed to be a straight line. It obviously passes a maximum and reaches the critical point with a negatively infinite derivative.

that if the known values of L at ordinary temperatures can be represented by a formula of the form

$$L = A\ (t_c - t)^n, \qquad n < 1,$$

one could also be sure that it gave correct values both for L and for dL/dt at the critical point, so that the use of the formula for other high temperatures would be, in a sense, an interpolation rather than an extrapolation. The constants can be determined and the formula tested in the range of the known L's by writting it in the logarithmic form

[31] Verh. Phys. Gesch., Berlin, 1897, **16**, 80.

$$\log L = n \log (t_c - t) + \log A.$$

That is, if $\log L$ is plotted against $\log (t_c - t)$ one should get a straight line. This turns out to be remarkably near the truth. Thiesen originally suggested $n = 1/3$; Henning [32] showed that his observations below 100° could be represented by putting $n = 0.31249$ and $A = 94.21$; a careful plot, a year ago, of the values available before the appearance of Henning's work above 100°, but including the values in Table I. in this paper, led to $n = 0.3150$ and $A = 92.93$. The work has been carefully repeated this fall. Including Henning's new work and the values in this paper, 37 values of L are available. They were

TABLE III.

Range.	No. of deviations.		Algebraic average of deviations in fractions of one per cent.
	+	−	
0°– 70°	2	9	−0.027%
70°–130°	14	0	+0.023%
130°–190°	4	8	−0.003% *
	37 = 20 + 17		

* This includes Henning's point at 181° with a deviation of +0.167% (see page 278); if this one point is omitted, the last value in the above table would be −0.018%.

plotted logarithmically on a large scale, and the slope of the line that best represented them was determined graphically by stretching a thread among the points. This was done several times by each of two different people, their results being closely accordant. The average of their values of n was then used to compute A arithmetically. The result is exactly the same as that of a year ago, namely,

$$L = 92.93\ (365 - t)^{0.3150}$$

The average of the numerical values of the differences between the 37 observed values of L and the numbers computed by means of the above formula is one fourteenth of one per cent, which is less than the probable accuracy of the measurements. It is true that there is some evidence of regularity among the deviations as the above table shows.

[32] Wied. Ann., 1906, **21**, 870.

These average deviations are, of course, very small, but the larger deviations in each group tend to cluster and to approach the limit of accuracy of the measurements, so that the systematic variation may be real. In any case, its amplitude is so small that it deserves but little consideration at this time.

4. Discussion of the Specific Heat of Superheated Steam.

It is the purpose of the rest of this paper to collect and revise such useful computations of other thermal properties of steam as are affected by a change in the accepted values of the total heat of saturated steam, together with such other results as are valuable for comparison with them. Section 4 will be concerned with the specific heat of superheated steam. Many papers on this subject have been published during the last ten years, especially in the technical press. They can be roughly classified under the following heads.

A. Direct experimental determinations.
B. Indirect experimental determinations and computations from other data.
   a. Throttling experiments.
   b. Computations based on characteristic equations or on volume measurements.
   c. Computations based on the Joule-Thomson effect.
   d. Computations along the saturation line based on Planck's equation.
   e. Other computations.
C. Resumes and discussions.

Each of these possible sources of information will be discussed in turn, with the object, not so much of reviewing previous papers, as of getting by each method the best information that the new material in this and in the preceding paper makes possible.

A. *Direct experimental determinations.* — Three of the papers that belong in this subsection have already been discussed in Section 2. The conclusion there reached was that of the three, that of Knoblauch, Linde and Klebe was the most reliable. Their results will therefore be used as the point of departure of this section, it being the object of each subsection, either to test the justice of the decision that their work is preferable to Thomas', or to determine what changes should be made in their curves to bring them nearer to the truth.

The most famous of all contributions to this subject is Regnault's direct experimental determination of C_p in 1862.[33] It seems not to be

[33] Mem. Inst. de France, 1862, **26**, 167.

generally known that his computations involve one step which modern work has shown to be erroneous. He made four sets of experiments, all at atmospheric pressure, and all covering about the same range of superheat. In each experiment, first slightly superheated steam, and later highly superheated steam at the same pressure, was condensed in a water calorimeter. The heat released per gram of steam in the first process was then subtracted from that released per gram of steam in the second process and the difference divided by the difference in superheat to give C_p. The results which he deduced from his experiments will be found in the third column of Table IV. below.

The error which he made was in the determination of the quantity

TABLE IV.

A Recomputation of Regnault's Values of C_p.

	Temp. range ($C°$).	R's value of C_p.	New value of C_p.	Kn's value of C_p.
Series 1	127.7–231.1	(0.46881) *	(0.4655) *	0.462
Series 2	137.7–225.9	0.48111	0.4769	0.462
Series 3	124.3–210.4	0.48080	0.4736	0.462
Series 4	122.8–216.0	0.47963	0.4780	0.462
Mean of last three . . .		0.48051	0.4762	

* ". . . les résultats de la première série, qui m'inspirent moins de confiance que les autres. . . ." Regnault, p. 178.

of water in his calorimeter. This he accomplished, not by weighing, but by a volumetric measurement in a sheet iron tank filled each time to a scratch on the glass tube that formed its neck. Regnault knew that the coefficients of expansion of the water and of the tank were such that the tank would hold fewer grams of water at the room temperatures at which he worked than at 0°, the temperature at which he had calibrated the tank. But he supposed that he also knew the specific heat of water to be an increasing function of the temperature at room temperatures as well as above 100° where he had carefully studied it. He therefore neglected both temperature changes, thinking that they neutralized each other, and used at all room temperatures the weight that would have filled the tank at 0°, and the specific heat 1.

We now know that the specific heat of water decreases with increasing temperature from 0° to above 25°. There is some difference of opinion between Barnes and Dieterici, the two leading investigators of the subject, as to the exact shape of the curve of variation, but it is near enough to the truth to take, as in the steam tables already mentioned, a mean curve between that of Barnes and that of Dieterici, giving the former twice the weight of the latter.

Regnault's values of C_p have been recomputed from the data in his memoir, using his own value for the coefficient of expansion of sheet iron, modern data for the density of water, and the mean curve just mentioned for the specific heat of water. The new results are given in the fourth column of Table IV. They are somewhat lower than his original values and are thereby brought nearer to the corresponding values obtained by Knoblauch and Jakob, which are given in the fifth column of the table.

In the present unsettled state of our knowledge of C_p, Regnault's work should have considerable weight.

The only other important direct experimental determination of C_p is that of Holborn and Henning.[34] Their work, like Regnault's, was only at atmospheric pressure, but, unlike his, it covered a very wide temperature range, reaching 1400° C. It is certainly to be regarded as standard in the region of high superheats. It shows that in that region C_p increases with increasing temperature, but not as rapidly as Knoblauch's curves would indicate.

In a "Memorandum by the Chief Engineer for the year 1906 to the Executive Committee of the Manchester Steam Users Association,"[35] the National Physical Laboratory at Teddington, England, is said to have found $C_p = 0.532$ at saturation at 4.3 atmospheres (147° C.). This value lies remarkably close to Knoblauch's saturation curve.

Ba. *Throttling experiments.* — The failure of even the best throttling experiments to give satisfactory values of C_p by the ordinary methods has already been mentioned. A new method elaborated by Dodge[36] is much more promising, but no thoroughly reliable results have yet been obtained by it.

Bb. *Characteristic equations:* — If a sufficiently accurate characteristic equation, $f(p, v, t) = 0$, were known for superheated steam, much useful information about C_p could be obtained from Clausius's equation

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial t^2}\right)_p.$$

[34] Ann., 1907, **23**, 809.
[35] Manchester, June 4, 1907.
[36] Proc. Am. Soc. Mech. Engs., 1907, **28**, 1265 and 1908, **30**, 1227.

At the present time this is not a good way to get information about C_p for two reasons. In the first place, all of the most reliable set of volume measurements yet made (Knoblauch, Linde and Klebe) lie close to the saturation line, not one of them reaching either 50° of superheat or 190° of temperature. No characteristic equation based on them can be depended on at points far out in the superheated region. And in the second place, Clausius' equation involves a second derivative of the observed quantity v, and even the first derivative of an empirically determined function is liable to relative errors much

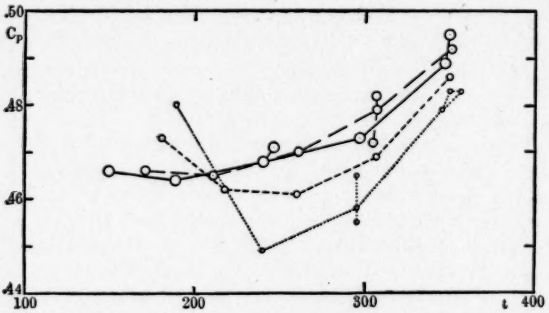

FIGURE 9. Knoblauch and Jakob's measurements of C_p, reduced to a pressure of 1 kg. per sq. cm. by means of Clausius' equation, using the characteristic equation developed by Linde to represent the volume measurements of Knoblauch, Linde, and Klebe. The smallest circles correspond to the highest original pressure (8 kg.), the next smallest to 6 kg., and so on. The progressive departure from a single curve with increasing pressure is marked.

larger than any in the observed quantity itself, while a second derivative is still more uncertain. This is illustrated by the fact that a characteristic equation of Tumlirz's form, which was shown by Linde to represent Knoblauch's volume measurements within four fifths of one per cent throughout their range, leads through Clausius' equation to the startling result that C_p does not vary at all with pressure at constant temperature, whereas it is known to vary within that same range by something like 60 per cent of its initial value.

The contention that even the best possible representation of Knoblauch's volume measurements is still too inaccurate to give reliable values of C_p, through Clausius' equation, can be further substantiated by an examination of the experimental data already described. Knoblauch and Jakob made observations on C_p at four pressures, all greater

than one atmosphere. If these are all "reduced" to one atmosphere by means of Clausius' equation, using Linde's best characteristic equation to represent the volume measurements, the results, plotted in Figure 9, show deviations from a common curve that increase with the pressure. The same is more strikingly true in Thomas' case. If his results, so recomputed [37] as to partly eliminate the wet steam error already mentioned (see page 271), are similarly reduced to one atmosphere by means of Clausius' thermodynamic equation and Linde's best characteristic equation, the progressive departure with increasing pressure from the probable curve for one atmosphere is very marked, the 500 lb. and 600 lb. values disappearing beyond the bottom of the diagram altogether. That is, although Linde's second best equation gave no variation of C_p with pressure at all, his best one gives altogether too much. The experimental evidence is thus wholly against the reliability of any C_p values obtained by means of Clausius' equation from any volume measurements as yet available.

Bc. *The Joule-Thomson effect.* — There are three ways in which C_p can be connected with the Joule-Thomson coefficient μ. The first of these was suggested almost simultaneously by Linde and by Planck.[38] It is thermodynamically rigorous, except for the assumption of the form of an analytical expression for μ as a function of t. The one they used, namely,

$$\mu = \frac{Const.}{T^2},$$

was proposed by Joule and Thomson in their original memoir on air, and is not at all accurate, especially for steam. If it is replaced by a more complicated expression, the integration of the partial differential equation, to which the reasoning of Linde and Planck leads, is impossible.

A second equation connecting C_p with μ is used by Griessmann [39] in the discussion of his throttling experiments. It is not a thermodynamic equation in the true sense because it does not involve either of the two laws of thermodynamics; it is merely a manipulative identity that can be proved by the laws of partial differentiation — that is a truism. It says that at any point in any thermodynamic plane

---

[37] Davis Proc. Am. Soc. Mech. Engs., 1908, **30**, 1433.

[38] Linde, Sitzungsber, bays. Akad., Math. Kl., 1897; Planck, "Vorlesungen über Thermodynamik," 1897, 117; Eng. ed., 1903, 124.

[39] Forschungsarb., 1904, **13**, 7 and 46.

$$C_p = \frac{(\partial H/\partial t)}{1 - \mu(\partial p/\partial t)}$$

provided only that both derivatives are taken in the same direction from the point. Griessmann uses the equation over the whole plane, but makes certain experimentally deduced assumptions which do not now seem to be justified.

The equation is likely to be most useful along the saturation line where dH/dt and dp/dt are both well known. Unfortunately μ is not as yet well known at such low temperatures, and it will be interesting to see whether, in the development of the subject, Griessmann's truism turns out to be more useful for the computation of C_p at saturation from μ or of μ from C_p.

The only use that will be made of the equation in this paper is to deduce from it the well-known theorem, usually attributed to Rankine, that at ordinary temperatures C_p at saturation must be numerically greater than dH_{sat}/dt.[40] At most temperatures this condition is so overwhelmingly fulfilled as to be of no value. At 0°C. it requires that C_p at saturation be as great as 0.44. Now if Knoblauch's saturation curve is continued to temperatures below 100° C., this condition will be found to require, either that the curve passes a minimum between 100° and 0°, or that it must lie somewhat higher between 100° and 150° so as to approach smoothly the right value at 0°. The existence of such a minimum has several times been suspected as a result of other indirect computations, and its experimental verification would be a matter of some interest; in the mean time the other alternative seems more probable, especially as it brings Knoblauch's values of C_p at atmospheric pressure into better agreement with Regnault's. Additional confirmation of this decision will be found on pages 293 and 300.

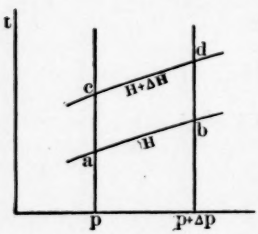

FIGURE 10.

The third of the methods referred to above for connecting C_p with μ is apparently new. It involves an equation which, like Griessmann's, is merely a manipulative identity or truism. It can be developed as follows. In Figure 10, let *ab* and *cd* be parts of two throttling curves on the usual *tp* diagram, the corresponding values of the total heat being H and $H + \Delta H$. Then at the pressures p and $p + \Delta p$ we have

[40] This follows at once from the fact that both μ and C_p are known to be positive.

$$C_p = \lim_{\Delta H \doteq 0} \frac{\Delta H}{t_c - t_a} \quad \text{and} \quad C_{p+\Delta p} = \lim_{\Delta H \doteq 0} \frac{\Delta H}{t_d - t_b},$$

from which

$$\frac{C_{p+\Delta p} - C_p}{C_p} = \lim_{\Delta H \doteq 0} \left[\frac{t_c - t_a}{t_d - t_b} - 1 \right].$$

Now, except for terms of higher order than ΔH and Δp,

$$t_b = t_a + \mu \Delta p,$$

$$t_d = t_c + \left[\mu + \left(\frac{\partial \mu}{\partial t} \right)_p (t_c - t_a) \right] \Delta p,$$

$$(t_d - t_b) = (t_c - t_a) \left[1 + \left(\frac{\partial \mu}{\partial t} \right)_p \Delta p \right].$$

Substituting this above gives

$$\frac{C_{p+\Delta p} - C_p}{C_p} = \lim_{\Delta H \doteq 0} \left[\frac{-\left(\frac{\partial \mu}{\partial t} \right)_p \Delta p}{1 + \left(\frac{\partial \mu}{\partial t} \right)_p \Delta p} \right]$$

and the limit sign is no longer necessary. Dropping it, dividing by Δp, and then letting Δp approach zero, gives

$$\frac{1}{C_p} \left(\frac{\partial C_p}{\partial p} \right)_H = - \left(\frac{\partial \mu}{\partial t} \right)_p.$$

Integrating this at constant H gives as the final equation [41]

$$C_p = C_{p_0} \epsilon^{-\int_{p_0}^{p} \left(\frac{\partial \mu}{\partial t} \right)_p dp}.$$

---

[41] The differential form of this equation can also be proved analytically as follows: For any three related quantities p, t, and H, one has the identity

$$\left(\frac{\partial p}{\partial t} \right)_H \left(\frac{\partial t}{\partial H} \right)_p \left(\frac{\partial H}{\partial p} \right)_t = -1.$$

But

$$\left(\frac{\partial t}{\partial p} \right)_H = \mu \text{ and } \left(\frac{\partial H}{\partial t} \right)_p = C_p,$$

and therefore

$$C_p = -\frac{1}{\mu} \left(\frac{\partial H}{\partial p} \right)_t. \qquad (1)$$

But for any function such as C_p which can be expressed in terms of any two of the variables p, t, and H, one has a second identity

$$\left(\frac{\partial C_p}{\partial p} \right)_H = \left(\frac{\partial C_p}{\partial p} \right)_t \left(\frac{\partial p}{\partial p} \right)_H + \left(\frac{\partial C_p}{\partial t} \right)_p \left(\frac{\partial t}{\partial p} \right)_H,$$

This formula has the disadvantage, as compared with Griessmann's, of involving the derivative of the inaccurately known function μ. This prohibits its use at the low temperatures close to saturation where μ is scarcely known at all, but makes much less difference at very high temperatures where the CO_2 points of Figure 5 of the preceding paper help to place the $\mu = f(t)$ curve with great definiteness. This method of computation is therefore at its best where many others fail completely.

The use of the new equation at ordinary temperatures is a matter requiring patience and much labor. First one computes and plots against t the derivative of the $\mu = f(t)$ curve of the preceding paper. Next one computes from the curve of μ itself the progress of some curve of constant H across the $p\ t$ plane; this is necessary so as to be able to express $\partial\mu/\partial t$ as a function of p in the integral. Then the integral has to be evaluated, either by replotting $\partial\mu/\partial t$ against p for the particular H curve in question and using an integraph, or by a step by step numerical process. The results are the Naperian logarithms of the desired ratios.

This process has been carried through for four curves in the region of moderate superheats. The results, which are presented in the first part of Table V., are in general in substantial agreement with the corresponding ratios computed from Knoblauch's curves, which are given in

---

Or
$$\left(\frac{\partial C_p}{\partial p}\right)_H = \left(\frac{\partial C_p}{\partial p}\right)_t + \mu\left(\frac{\partial C_p}{\partial t}\right)_p. \tag{2}$$

Now from the definition of C_p

$$\left(\frac{\partial C_p}{\partial p}\right)_t = \left(\frac{\partial}{\partial p}\right)_t \left(\frac{\partial H}{\partial t}\right)_p = \frac{\partial^2 H}{\partial p \partial t}, \tag{3}$$

and from (1)

$$\left(\frac{\partial C_p}{\partial t}\right)_p = -\frac{1}{\mu}\frac{\partial^2 H}{\partial t \partial p} + \left(\frac{\partial H}{\partial p}\right)_t \frac{1}{\mu^2}\left(\frac{\partial \mu}{\partial t}\right)_p. \tag{4}$$

Substituting (3) and (4) in (2) and using (1) gives the desired equation. Neither of the laws of thermodynamics has been used.

The differential form of the equation can also be deduced immediately from the equation

$$\left(\frac{\partial C_p}{\partial p}\right)_t = -\left(\frac{\partial(\mu C_p)}{\partial t}\right)_p$$

which Grindley proves on pages 31 and 32 of his paper in the Philosophical Transactions. His proof depends twice over on each of the two laws of thermodynamics, but it need not have, as the above derivations show. The use which he makes of his form of the equation is quite different from that here proposed.

the last of each set of columns. The chief disagreement is along curve 1 where Knoblauch's curves are too condensed. This means either that his curve at atmospheric pressure should be lower, or that the lower part of his saturation curve, with the constant pressure curves near it, should be higher. The first of these possibilities would mean even less agreement between Knoblauch and Regnault than at present, and may therefore be rejected. The remaining possibility has already been suggested by the result obtained from Griessmann's truism (see page 290). Furthermore, it will be corroborated again in the next section (see page 300). It may therefore be accepted the more readily here.

At very high superheats, where the method is most valuable, the

TABLE V.

C_p Ratios obtained from the Joule-Thomson Effect.

Press. kg./sq. cm.	Curve 1.			Curve 2.			Curve 3.		
	Temp.	C_p/C_{p_0}	Kn.	Temp.	C_p/C_{p_0}	Kn.	Temp.	C_p/C_{p_0}	Kn.
0.1	121.3	0.946	0.97	149.0	0.960	0.98	204.5	0.984	0.98
0.5	123.3	0.970	0.98	150.5	0.979	0.99	205.4	0.991	0.99
1.0	125.8	1.000	1.00	152.3	1.000	1.00	206.4	1.000	1.00
1.5	128.2	1.030	1.02	154.0	1.020	1.02	207.5	1.009	1.01
2.0	130.6	1.060	1.03	155.8	1.041	1.03	208.5	1.018	1.02
2.5	132.9	1.090	...	157.5	1.062	...	209.5	1.026	...
3.0	135.1	1.120	1.07	159.1	1.082	1.06	210.5	1.034	1.04
3.5	137.2	1.150	...	160.7	1.102	...	211.5	1.043	...
4.0	...	...	...	162.3	1.122	1.10	212.5	1.051	1.06
5.0	...	...	...	165.5	1.161	...	214.5	1.067	...
6.0	...	...	...	168.5	1.200	1.17	216.5	1.084	1.09
7.0	...	...	...	171.4	1.237	...	218.4	1.101	...
8.0	...	...	...	174.3	1.264	1.25	220.2	1.118	1.12
9.0	...	...	...	177.0	1.309	...	222.1	1.135	...
10.0	...	...	...	179.7	1.344	1.34	223.9	1.151	1.15
12.0	...	...	...	...	...	...	227.5	1.183	...
14.0	...	...	...	...	...	...	230.9	1.215	...
16.0	...	...	...	...	...	...	234.3	1.246	...
18.0	...	...	...	...	...	...	237.6	1.277	...
20.0	...	...	...	...	...	...	240.9	1.307	...
22.0	...	...	...	...	...	...	244.1	1.337	...
24.0	...	...	...	...	...	...	247.2	1.367	...
26.0	...	...	...	...	...	...	250.3	1.396	...
28.0	...	...	...	...	...	...	253.4	1.424	...

TABLE V — *continued.*

Press, kg./sq. cm.	Curve 4.			Curve 5, near 485° C.	Curve 6, near 600° C.	Curve 7, near 925° C.	Curve 8, near 1480° C.
	Temp.	C_p/C_{p_0}.	Kn.	C_p/C_{p_0}.	C_p/C_{p_0}.	C_p/C_{p_0}.	C_p/C_{p_0}.
0.1	287.8	0.994	0.99	...	...	...	...
1.0	288.9	1.000	1.00	1.0000	1.0000	1.0000	1.0000
2.0	290.1	1.007	1.01	1.0025	1.0016	1.0009	1.0004
4.0	292.4	1.020	1.025	1.0053	1.0036	1.0020	1.0010
6.0	294.7	1.032	1.035	1.0082	1.0055	1.0031	1.0015
8.0	297.0	1.044	1.045	1.0106	1.0072	1.0041	1.0019
10.0	299.2	1.057	1.055	1.014	1.009	1.005	1.002
12.0	301.4	1.069	...	1.016	1.011	1.006	1.003
14.0	303.6	1.081	...	1.019	1.013	1.007	1.003
16.0	305.8	1.093	...	1.022	1.015	1.008	1.004
18.0	308.0	1.105	...	1.025	1.017	1.009	1.004
20.0	310.1	1.117	...	1.028	1.019	1.011	1.005
22.0	313.3	1.128	...	1.030	1.020	1.012	1.005
24.0	314.4	1.140	...	1.033	1.022	1.013	1.006
26.0	316.4	1.151	...	1.036	1.024	1.014	1.006
28.0	318.5	1.163	...	1.039	1.026	1.015	1.007

computation is simpler for two reasons. In the first place, μ and $\partial\mu/\partial t$ are both so small that the temperature can be assumed constant along a curve of constant H. $\partial\mu/\partial t$ is then constant in the integration. And in the second place $\partial\mu/\partial t$ can be computed from Buckingham's[42] equation for μ' against t', both in reduced units, namely,

$$\mu' = \frac{0.209}{t' - 0.32} - 0.0368.$$

This is corrected for the fact that although, in his paper, 100 inches of mercury is taken as the unit of pressure, his critical pressures are expressed in atmospheres. It was shown in the preceding paper that this equation can safely be assumed to hold for steam at very high superheats, since it is known to hold for the other gases which Buckingham discusses, and they are known to be connected with steam by a law of corresponding states.

This simpler process has been carried through for the four very high temperatures mentioned in the last part of Table V, with the results there presented. These results are the basis of the high superheat part of the Steam Tables of Marks and Davis.

[42] Bul. Bureau of Standards, 1907, **3**, 263.

Bd. *Planck's equation* : — There remains the most interesting of all the indirect attacks on C_p at ordinary temperatures. In 1897 Planck published in his thermodynamics the equation

$$c_p = \frac{dH}{dt} - \frac{L}{T} + \frac{L}{u}\left[\left(\frac{\partial v}{\partial t}\right)_{p_{(\text{steam})}} - \left(\frac{\partial v}{\partial t}\right)_{p_{(\text{water})}}\right].$$

This equation holds only along the saturation curve. For its derivation the reader is referred to the English translation of Planck's book[43] or to Griessmann's paper.[44] The two partial derivatives must be such as to describe the behavior of superheated steam and of water, both close to the steam dome, not of steam within the steam dome. In practise, the second of these derivatives is always negligible in comparison with the first.

Two sorts of experimental material are necessary for computations with this equation, a set of total heat values (those proposed in this paper will be used), and a set of values of $(\partial v/\partial t)_p$ for superheated steam close to saturation. The latter can be based on the volume measurements of Knoblauch, Linde and Klebe,[45] or on those on Ramsay and Young,[46] or on those of Battelli.[47] These three sources will be considered in turn.

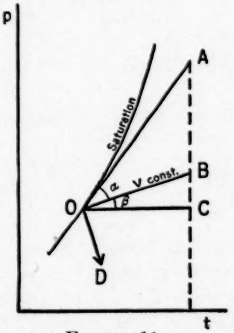

FIGURE 11

In the experiments of Knoblauch, Linde, and Klebe, the volume was held constant while the pressure and temperature were varied. Their results, when plotted on the p t plane, gave isochors or lines of constant volume. These turned out to be straight lines within the limit of error of the measurements. Their slopes are entered with other data in the main table of the original paper. These slopes are values of $(\partial p/\partial t)_v$ and some manipulation is necessary to get from them the desired values of $(\partial v/\partial t)_p$. Let Figure 11 represent a portion of the p t plane drawn, like an analytical geometry figure, with the same unit of length along each axis. Then

[43] Treatise on Thermodynamics, 1903, 147.
[44] Forschungsarb., 1904, **13**, 8.
[45] Forschungsarb., 1905, **21**, 33. [46] Phil. Trans., 1893, **183** A, 107.
[47] Mem. di Torino, 1893, **43**, 63; condensed in Ann. Chim. et Phys., 1894, **3**, 408.

$$\tan(\alpha+\beta)=\left(\frac{\partial p}{\partial t}\right)_{\text{sat.}}.$$

This derivative is well known from the work of Holborn and Henning.[48] Also

$$\tan\beta=(\partial p/\partial t)_v.$$

This is the derivative given by Knoblauch, Linde, and Klebe, as just explained. Along OB, v is constant; along OD, which is perpendicular to OB, v increases most rapidly. The following equations can then be verified, "Grad. v" being the space rate of v's increase along OD.

$$\text{Grad. } v=-\frac{1}{\sin\alpha}\frac{v_A-v_0}{\overline{OA}}.$$

$$\left(\frac{\partial v}{\partial t}\right)_p=\lim_{\Delta t\doteq 0}\frac{v_c-v_0}{\Delta t}=\lim_{\Delta t\doteq 0}\frac{\overline{OC}\cdot\text{Grad. } v\cdot\sin\beta}{\Delta t}$$

$$=-\frac{\sin\beta}{\sin\alpha}\frac{\overline{OC}}{\overline{OA}}\lim_{\Delta t\doteq 0}\frac{v_A-v_0}{\Delta t}$$

$$=-\frac{\sin\beta}{\sin\alpha}\cos(\alpha+\beta)\left(\frac{\partial v}{\partial t}\right)_{\text{sat.}}$$

The last term of Planck's equation can then be written in the form

$$\frac{L}{u}\left(\frac{\partial v}{\partial t}\right)_{p_{(\text{steam})}}=AT\left(\frac{dp}{dt}\right)_{\text{sat.}}\left(\frac{\partial v}{\partial t}\right)_p=-AT\left(\frac{\partial v}{\partial t}\right)_{\text{sat.}}\frac{\sin(\alpha+\beta)\sin\beta}{\sin\alpha}.$$

In this transformation use has been made of the familiar Clapyron equation and of the definition of $\tan(\alpha+\beta)$. The computations are carried through by determining $(\alpha+\beta)$ and β from their tangents and getting α by subtraction. The necessary values of the differential coefficient $(\partial v/\partial t)_{\text{sat}}$ were formed from the values of v in the Steam Tables of Marks and Davis by the usual finite difference formula

$$dv=\Delta v-\tfrac{1}{2}\Delta_2 v+\ldots\ldots$$

The results of the computation are summarized in the first part of Table VI., and are plotted as black dots in Figure 12.

[48] Wied. Ann., 1908, **26**, 835.

The necessary values of $(\partial v/\partial t)_p$ can also be obtained by differentiating the complicated characteristic equation which Linde has developed

TABLE VI.

VALUES OF C_p AT SATURATION FROM PLANCK'S EQUATION, USING:
a. KNOBLAUCH, LINDE, AND KLEBE'S EXPERIMENTAL DATA. *b.* LINDE'S CHARACTERISTIC EQUATION.

Temp.	C_p.	Temp.	C_p.	Temp.	C_p.	
					Knoblauch.*	Thomas.*
101.4	0.46	140.9	0.54	100.6	0.484	0.519
102.4	0.55	143.0	0.65	126.3	0.506	0.533
108.1	0.44	143.2	0.52	153.1	0.560	0.585
110.7	0.56	144.1	0.52	170.1	0.615	0.634
112.4	0.49	149.8	0.58	193.2	0.722	0.737
114.8	0.40	150.2	0.54	205.1	0.794	0.808
115.3	0.36	153.7	0.56	215.8	0.875	0.885
119.1	0.50	154.2	0.60	225.1	0.956	0.966
119.3	0.52	157.6	0.56	235.8	1.067	1.075
122.1	0.49	159.6	0.58	245.2	1.179	1.184
122.6	0.53	163.7	0.64	253.5	1.293	1.298
126.3	0.49	166.0	0.59			
131.5	0.53	170.0	0.58			
131.9	0.51	174.6	0.62			
133.0	0.47	180.8	0.64			
139.1	0.53	183.0	0.66			

* The column headed "Knoblauch" is based on the H formula of this paper. That headed "Thomas" is based on a modified H formula derived from his values of C_p. It is inserted only for comparison with the preceding one (see page 299). In both columns values above 200° involve a doubtful extrapolation of Linde's equation beyond its proper range. All temperatures are on the centigrade scale.

TABLE VI — *continued.*

VALUES OF C_p AT SATURATION FROM PLANCK'S EQUATION, USING:
c. RAMSAY AND YOUNG'S EXPERIMENTAL DATA. *d.* BATTELLI'S "TABLE M."

Temp.	C_p.	Temp.	C_p.
130.3	0.69	99.5	0.46
133.2	0.69	129.9	0.42
136.9	0.60	133.9	0.48
144.3	0.72	140.6	0.49
154.1	0.74	143.8	0.50
168.2	0.64	149.2	0.50
180.4	1.04	160.9	0.49
191.3	0.80	178.5	0.48
		180.9	0.54
		192.0	0.55
		199.0	0.59

to represent the same data. This alternative computation seems worth while, partly because of the automatic smoothing effect which the use of an equation based on all the observations necessarily has, but more because it means a redistribution of the dependence of the computed values of C_p on the volume measurements on the one hand and the new H formula on the other. The results of eleven computations of this kind are summarized in the second part of Table VI., and five of them are plotted as circles in Figure 12.

Two conclusions can be drawn from Figure 12. In the first place, both sets of points agree in confirming the conclusion reached on page 272, that Knoblauch's saturation curve is nearer the truth than Thomas'. It will probably be argued this confirmation is simply a circular fallacy, inasmuch as the H formula of this paper was based on Knoblauch's values of C_p and might therefore be expected to lead back to them in the end. This is true only in a very small measure. The dependence of H on C_p is such that comparatively large changes in the C_p curves used at the beginning of this paper would have made

only small changes in the H formula, C_p being a factor, not of H itself, but only of ΔH. And in the second part of the computation, the re-dependence of C_p on H is again insensitive to errors in the assumed function, which this time is H. All this can be strikingly illustrated as follows. It is easy to compute approximately by the method of Section 3 of this paper a value of ΔH near 140° and one near 180° using Thomas' values of C_p instead of Knoblauch's. These, with

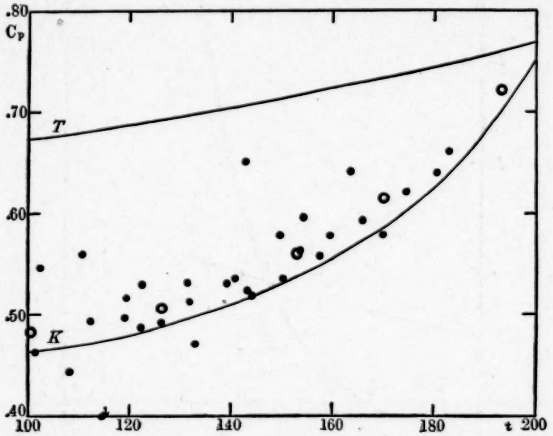

FIGURE 12. Values of C_p computed by Planck's method. The dots are based on the original volume measurements of Knoblauch, Linde and Klebe; the circles are based on Linde's characteristic equation. The lower curve is Knoblauch's saturation line; the upper one is Thomas'.

$\Delta H = 0$ at 100°, give a new second degree equation for $H = f(t)$ based wholly on Thomas' values. Finally this new H equation can be used with Linde's characteristic equation to compute, by means of Planck's equation, a set of values of C_p at saturation which are exactly comparable with those in the second part of Table VI., except that Knoblauch's C_p work is wholly replaced by Thomas'. If there is a circular fallacy in the confirmation mentioned at the beginning of this paragraph, the new results ought to confirm Thomas' C_p values at saturation just as definitely as the old ones did Knoblauch's. As a matter of fact, this is not at all the case. The new results are compared with the old in Figure 13, and agree strikingly in confirming Knoblauch's saturation curve. In other words, no matter which set of C_p values

one starts with, one is led by this method of successive approximations to something much like Knoblauch's curve in the end.

The second conclusion that can be drawn from Figure 12 is that the true saturation curve, although close to Knoblauch's curve, probably runs somewhat higher in the range covered by these computations.

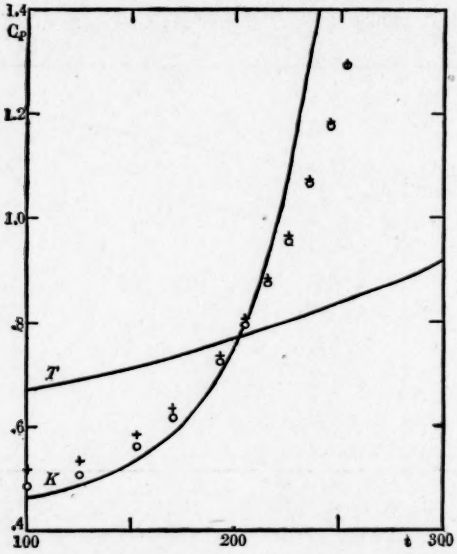

FIGURE 13. Values of C_p computed by Planck's method from Linde's characteristic equation. The circles come from an H formula based wholly on Knoblauch's C_p measurements, the crosses from a similar H formula based wholly on Thomas' C_p measurements. Both confirm Knoblauch's saturation curve (K) rather than Thomas' (T).

It will be remembered that the same conclusion was reached in two different ways in the last subsection (pages 290 and 293), and that it is further confirmed by the fact that Regnault's values near saturation at atmospheric pressure are higher than Knoblauch's.

The volume measurements of Ramsay and Young and of Battelli are not so conveniently arranged for the purposes of this particular computation. In both cases the temperature was held constant while the pressure and volume were varied. In the case of Ramsay and Young it is possible to rearrange the data so as to give approximate isochors

which can then be reduced to suitable absolutely constant volumes by interpolation. The curves thus obtained are, however, irregular, and furthermore they show unmistakable evidences of a phenomenon exactly analogous to the wet steam error into which Thomas is believed to have fallen. The presence of this error, which took the form of surface condensation in the experimental bulb as saturation was approached, is specifically mentioned by the authors, but no attempt was made to eliminate it on the ground that, "however interesting

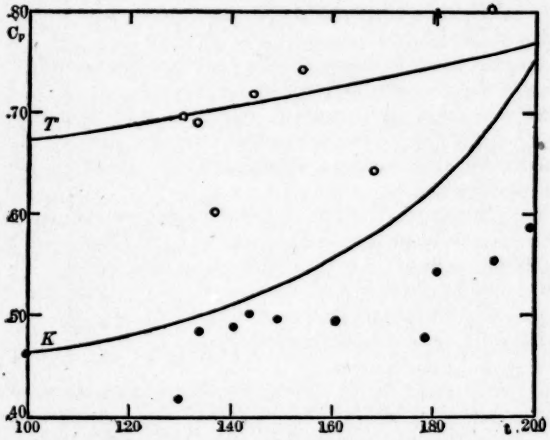

FIGURE 14. Values of C_p computed by Planck's method from the volume measurements of Ramsay and Young (circles) and of Battelli (dots).

from a theoretical point of view the absolute expansion of water-gas may be, in practise it is always in contact with a surface; and an indication of the behavior of steam in contact with glass cannot fail to be of use in considering the practical case of steam in contact with iron." It is therefore interesting to find that the values of C_p which have been computed from the data of Ramsay and Young and which are plotted as circles in Figure 14, run close to Thomas' saturation curve. This agreement is an indication that both are subject to the same error.

Battelli was also troubled by surface condensation, but was at great pains, in discussing his results, to eliminate its effects. It has therefore seemed best to work not from his data, but from a table near the

end of his memoir ("Table M"), in which are given certain graphically determined values of the coefficients in the formula

$$p = b\,t + a,$$

which he, like Knoblauch, Linde, and Klebe, uses to represent his isochors. The coefficient b in this formula is the same as the $(\partial p/\partial t)_v$ in the main table of Knoblauch's paper, and can be used in the same way. The values of C_p computed from Battelli's table M with condensation effects eliminated, run even lower than Knoblauch's saturation curve throughout the range of Figure 14. This indicates that Battelli rather more than eliminated the condensation errors in his discussion of his data.

The contrast between the values obtained from Ramsay and Young's work, where the wet steam error is known to exist, and those obtained from Battelli's work, where it is known to have been consciously eliminated, is so much like the contrast between Thomas' saturation curve and Knoblauch's as to be a striking verification of the conclusion reached on page 272.

It is not probable that either of the three sets of volume measurements are reliable enough to make the results computed in this section worthy of much consideration as new determinations of C_p. Their value is chiefly as corroborative evidence on one side or the other of the various doubtful points that have been mentioned.

Be. *Other indirect computations.* —
C. *Resumes and discussions.* — } None of the papers which might be listed under Be or C are such as to be improvable by the use of the new material in this and in the preceding paper, or to be of importance in the present connection. They will not be discussed in detail.

Summary of this C_p discussion: —

1. Knoblauch's curves in general, and his saturation curve in particular, are much nearer the truth than Thomas'. The evidence for this is to be found on pages 287 and 298 to 302.

2. Knoblauch's saturation curve runs somewhat too low at low temperatures (see pages 290, 293 and 300).

3. The low temperature end of Knoblauch's 1 kg. curve should be somewhat raised, not only because of conclusion 2 above, but also so as to agree better with Regnault's recomputed results (see page 286).

4. Knoblauch's 1 kg. curve should be relocated at high superheats so as to agree with that of Holborn and Henning.

5. The spacing at high superheats of the curves corresponding to pressures higher than 1 kg. is best determined by a new method involving the Joule-Thomson coefficient (see pages 290 to 294).

6. The reconciliation, through Clausius' thermodynamic relation, of the accepted volume and specific heat measurements in the superheated region is impossible. This is probably the most important of the outstanding problems in this field.

All these conclusions have been embodied in the C_p diagram which is the basis of the Steam Tables already mentioned,[49] and it is partly for the purpose of gathering in one place all of the underlying evidence that justifies those tables, much of it unsuitable for presentation there, that this section of the present paper has been written. The C_p curves which were used were as faithful a translation and extrapolation of Knoblauch's curves as possible, except for the differences stated above. In particular they reproduced the tremendous rise of his saturation curve at even moderately high pressures and temperatures. It is probable that this feature of Knoblauch's curves, although near enough to the truth to satisfy the present needs of engineering practise, will have to be revised later. It is, however, the only rational guess yet published, and it is not worth while to cumber the literature with any more "harmonized" sets of C_p values at high pressures until there is something definite to build on. The problem of determining the true course of the high pressure end of the saturation curve on the C_p diagram is second in importance only to that mentioned at the end of the summary just above.

5. Clausius' "Specific Heat of Saturated Steam."

This section will be devoted to a revision of a computation first made by Clausius, which, although no longer of especial importance, is usually of considerable interest to students of thermodynamics. In the sixth chapter of the first volume of his "Mechanical Theory of Heat" he defines the specific heat of saturated steam as the quantity of heat that must be added to saturated steam at any temperature to turn it into saturated steam one degree hotter, account being taken of the fact that it will have to be compressed to keep it saturated. For steam and for most other substances it is negative at ordinary temperatures, because the work of compression is more than enough to provide the corresponding increase in the internal energy. But in the case of most substances including steam it is at ordinary temperatures an increasing function of the temperature and may, therefore, pass through zero and become positive if the temperature is sufficiently raised. This Clausius found to be actually the case for ether at ordinary temperatures and for chloroform above 130°, and the ex-

[49] See page 97 of the Tables.

periments of Cazin and of Hirn confirmed this result. For such substances, the top of the temperature-entropy diagram must have the curious shape shown in Figures 15*a* and 15*b*.

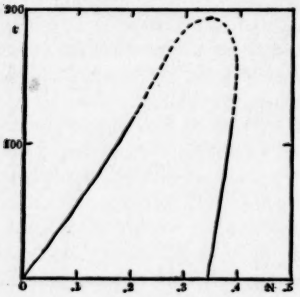

FIGURE 15*a*. Temperature-entropy diagram for ether.

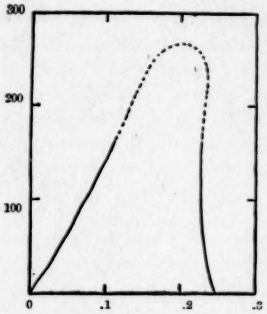

FIGURE 15*b*. Temperature-entropy diagram for chloroform.

The extrapolation formula for L in sub-section 3C enables one to compute this specific heat of saturated steam from Clausius' equation.

$$C_{\text{sat.}} = \frac{dL}{dt} + c - \frac{L}{T}$$

with the following results.

TABLE VII.

THE SPECIFIC HEAT OF SATURATED STEAM.

Temp.	$C_{\text{sat.}}$	Same acc. to Clausius.
0°	−1.69	−1.916
50°	−1.33	−1.465
100°	−1.08	−1.133
150°	−0.90	−0.879
200°	−0.80	−0.676
250°	−0.82	....
300°	−1.13	....

The necessary values of the specific heat of water, c, are taken from Marks and Davis' Steam Tables. Above 100° they are based on the experiments of Dieterici which run to 303°. The Table shows that $C_{sat.}$ passes its maximum below 250° without becoming zero or positive, and that at 300° it is already well on its way toward the value minus infinity which it has at the critical point. The temperature-entropy diagram for steam (see Figure 7*a*) is, therefore, fundamentally different in shape from that of ether or chloroform.

6. The Critical Volume of Water.

The extrapolation formula for L also makes possible a computation of the critical volume of water by the method of Cailletet and Mathias. These investigators announced in 1886[50] their well-known "law of the straight diameter," according to which, if the densities of a liquid and its saturated vapor are plotted against the corresponding temperatures to form a steam dome, the mid-points of the horizontal chords of the dome lie in a straight line. This law has been tested by a number of observers,[51] but particularly by Young, who proved that the diameter is accurately straight only in the case of a few "normal" substances of which normal pentane is the best known example, but that it is always nearly straight and can almost always be represented within the limit of error of the observations by a second degree equation in t. In certain cases, notably acetic acid and the alcohols, a third degree equation is necessary. All departures of the diameter from perfect straightness are commonly attributed to association in the liquid.

If the equation of the diameter is known, the substitution in it of the critical temperature gives the critical density with an accuracy far surpassing that of any known method of direct measurement. This accuracy is greatly increased by the fact that the diameter is always so nearly parallel to the t axis that even a considerable error in the critical temperature makes very little difference in the critical volume.

In applying this method to the determination of the critical density of water, one finds available in the third (1905) edition of Landolt and Bornstein's "Physikalische Tabellen" a satisfactory set of values

[50] C. R., 1886, **102**, 1202.

[51] Mathias, Ann. de la Fac. des Sci. Toulouse, 1892, **6**, M1; C. R., 1892, **115**, 35; Mém. Soc. Roy. des Sci., Liege, 1899, **2**; Journ. de Phys., 1899, **8**, 407; and 1905, **4**, 77; Young, Journ. Chem. Soc., trans., 1893, **63**, 1237; Phil. Mag., 1892, **34**, 503; and 1900, **50**, 291; Guye, Archives des Sci. Phys. et Nat., 1894, **31**, 43; Tsuruta, Phys. Rev., 1900, **10**, 116. See also Young's "Stoichiometry," 1908, 165.

of the density of water up to 320°C. Furthermore, the pressure of saturated steam has been observed up to the critical point itself by a number of observers, of whom Cailletet and Colardeau [52] seem the most trustworthy. From their values and the extrapolation formula for L, one can compute the change of volume during vaporization up

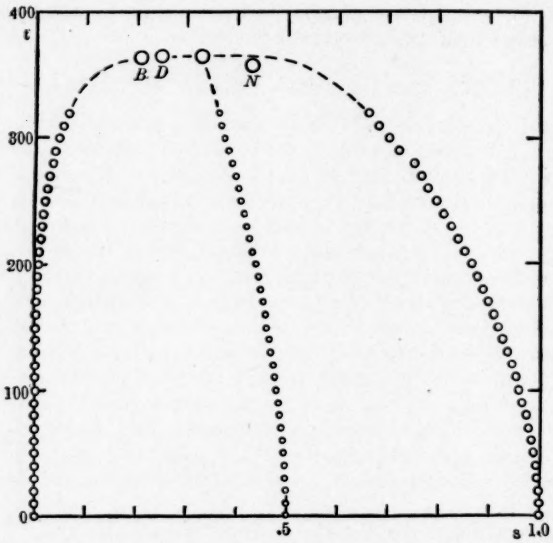

FIGURE 16. The steam dome on the temperature-density plane, with the "straight diameter" of Cailletet and Mathias, and the critical point according to Nadejdine (N), Battelli (B), Dieterici (D), and the present writer.

to 320° and indeed up to the critical point itself. The sum of these values and the volumes of the liquid mentioned above are the volumes of saturated steam up to 320°. The results are tabulated below and are plotted in Figure 16. The diameter is seen to be, as usual, nearly but not quite straight. It is not possible to represent the whole of it even by a third degree formula in t, because of the peculiar behaviour of the density of water at low temperatures. The 20 points above

[52] Journ. de Phys., 1891, **10**, 333; also Ann. Chem. et Phys., 1892, **25**, 519; also Physik. Rev., 1892, **1**, 14; also a short note in C. R., 1891, **112**, 563; see also Risteen, The Locomotive, 1907, **26**, 219.

TABLE VIII.

THE LAW OF THE STRAIGHT DIAMETER FOR STEAM.

Temp. C°.	Density of Water.	Density of Steam.	Mean Density.	Formula.	Diff.
0°	0.9999	0.000005	0.5000	...	...
10°	0.9997	...	0.4999	...	...
20°	0.9982	...	0.4991	...	...
30°	0.9957	...	0.4978	...	...
40°	0.9922	0.00005	0.4961	...	...
50°	0.9881	0.00008	0.4941	...	...
60°	0.9832	0.00013	0.4917	...	...
70°	0.9778	0.0002	0.4890	...	...
80°	0.9718	0.0003	0.4860	...	...
90°	0.9653	0.0004	0.4828	...	...
100°	0.9584	0.0006	0.4795	...	...
110°	0.9510	0.0008	0.4759	...	...
120°	0.9434	0.0011	0.4722	...	...
130°	0.9352	0.0015	0.4684	0.4688	+0.0004
140°	0.9264	0.0020	0.4642	0.4644	+0.0002
150°	0.9173	0.0026	0.4599	0.4599	0.0000
160°	0.9075	0.0033	0.4554	0.4552	−0.0002
170°	0.8973	0.0041	0.4507	0.4504	−0.0003
180°	0.8866	0.0052	0.4459	0.4454	−0.0005
190°	0.8750	0.0064	0.4407	0.4403	−0.0004
200°	0.8628	0.0079	0.4354	0.4351	−0.0003
210°	0.850	0.010	0.430	0.431	+0.001
220°	0.837	0.012	0.424	0.424	0.000
230°	0.823	0.014	0.419	0.419	0.000
240°	0.809	0.017	0.413	0.413	0.000
250°	0.794	0.020	0.407	0.407	0.000
260°	0.779	0.024	0.402	0.401	−0.001
270°	0.765	0.029	0.397	0.395	−0.002
280°	0.75	0.03(4)	0.39(2)	0.388	−0.00(4)
290°	0.72	0.03(9)	0.38(0)	0.382	+0.00(2)
300°	0.70	0.04(6)	0.37(3)	0.375	+0.00(2)
310°	0.68	0.05(5)	0.36(8)	0.368	0.00(0)
320°	0.66	0.06(5)	0.36(2)	0.362	0.00(0)

120° can, however, be represented with an average deviation of about one ninth of one per cent by the formula

$$s = 0.4552 - 0.0004757\ (t-160) - 0.000000685\ (t-160)^2 \text{ gr./cm.}^3$$

It should be noticed, in judging of the reliability of the formula, that comparatively large relative errors in the density of steam make only

very small relative errors in the mean of the densities. Thus in the most unfavorable case, at 320°, if an error in either dp/dt or in the extrapolated value of L made the computed change of volume wrong by five per cent, the resulting error in the mean of the densities would be less than half of one per cent.

The substitution of Cailletet and Colardeau's value for the critical temperature of water, $t_c = 365°$C., in the equation of the diameter gives

$$s_c = 1/v_c = 0.329 \text{ gr./cm.}^3,$$

from which it follows that the critical volume is

$$v_c = 3.04 \text{ cm.}^3/\text{gr.}$$

There are three previous determinations with which this can be compared, two of which are direct measurements. These are

$$v_c = 2.33 \text{ cm}^3/\text{gr. (Nad.)},$$

found by Nadejdine[53] in 1885, and

$$v_c = 4.812 \text{ cm.}^3/\text{gr. (Batt.)},$$

found by Battelli[54] in 1890. In both cases a known weight of water was enclosed in a steel tube and heated at constant volume until the contents became homogeneous. If there was too little liquid, this occurred when it was all evaporated; if too much, when it had so expanded as to fill the tube; if just enough, at the critical point. The last case they hoped to recognize because of its corresponding to a higher temperature than either of the others. Such a method gives an excellent determination of the critical temperature, but it can hardly be expected to give an accurate determination of the critical volume. It amounts to trying to find the highest point of the steam dome by selecting experimentally its longest ordinate on the v t plane. The extremely flat top of the steam dome makes this almost impossible, and it is interesting to notice that both Nadejdine and Battelli fell within the nearly flat region, one at one end and one at the other. The present determination lies between theirs and should be much more accurate than either.

---

[53] Universitatäkija Investia Kiew., 1885, **6**, 32; Mel. Phys. et Chim. tirés du Bull. de l'Ac. de St. Pétersb., 1885, **12**, 299; Chem. CBl., 1885, **17**, 401.

[54] Mem. dell. Ac. di Torino, 1891, **41**, 76; Physikal. Rev., 1892, **2**, 1.

The third published value of the critical volume,

$$v_c = 4.025 \text{ cm.}^3/\text{gr. (Diet.)},$$

was computed by Dieterici[55] in 1904, from the empirical law of Young[56] that, for "normal" substances, the ratio of the actual to the gas-law density at the critical pressure and density is 3.8. Dieterici's belief that water becomes a "normal" substance at high temperatures, even though it is known to be very abnormal at ordinary temperatures, is based on the fact that the ratio of the change of internal energy dur-

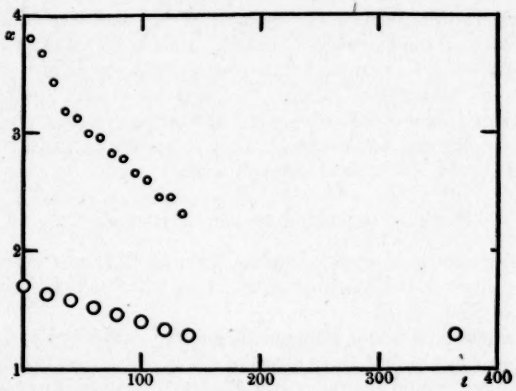

FIGURE 17. The polymerization factor for liquid water as a function of the temperature. The small circles below 150° are Ramsay's earlier values; the large circles below 150° are his revised values; the circle at 365° is the value indicated by the critical volume.

ing evaporation to the whole heat of evaporation, L, seemed to approach a value which he had predicted for "normal" substances. The present determination of v_c shows that water is, as one would have expected, still abnormal at the critical point. If interpreted in the usual way, it would indicate a polymerization factor of 1.3. Figure 17 shows how well this number fits a smooth curve through Ramsay's earlier large values of the polymerization factor at ordinary temperatures;[57]

[55] Wied. Ann., 1904, **15**, 864.

[56] Phil. Mag., 1892, 34, 507, and Jour. Chem. Soc., Papers, 1893, **63**, 1251.

[57] Phil. Trans., 1893, **184**A, 647; translated in Zeitsch. Phys. Chem., 1893, **12**, 433; second paper in Jour. Chem. Soc., 1893, **63**, 1089; translated in Zeitsch. Phys. Chem., 1893, **12**, 458.

there seems, however, to be little chance of reconciling it with his later "corrected" values.[58] This is an example of the uncertainty that seems to characterize the whole subject of polymerization in liquids, especially on its quantitative side.

The equation of the mean diameter which has just been obtained can also be used for the computation of a rough but useful extension of certain columns of the ordinary steam tables up to the critical point. As was mentioned on page 306, the extrapolation formula for L of Section 3 determines the change of volume during evaporation at all temperatures between 320° and the critical temperature. From these and the mean densities given by the equation of the diameter, it is easy to compute each of the densities separately, and to fill in the rest of the steam dome on the t s (temperature-density) planes. The results are shown by the dotted lines in Figure 16, and are given in detail at the end of Table I in the Steam Tables already mentioned. Any values obtained in this way are, of course, only rough approximations to the truth and should not be too much relied on.

Summary of the Results in this Paper.

1. It presents a new set of values for the difference between the total heat of saturated steam at certain temperatures between 65° and 190°C. and its value at 100°.

2. It shows that these differences can be represented within their limit of error by the first three terms of a Taylor's series, but that such a development should not be extrapolated far in either direction. The best direct measurements of H indicate that its value at 100° is 639.11 mean calories. If this be accepted, the proposed formula for H is

$$H = 639.11 + 0.3745\ (t - 100) - 0.000990\ (t - 100)^2 \text{ mean calories.}$$

The last two terms of the formula are the real contribution of this paper, and may still be valid, even if the first term is later found to be wrong.

3. Thiesen's formula for L with recomputed constants is shown to represent satisfactorily all of the reliable values of L, including those in this paper. It is believed to be the safest known means of extrapolating to high temperatures.

4. The literature on the specific heat of superheated steam is systematically discussed and revised in the light of the new values of H

[58] Third paper; Proc. Roy. Soc., 1894, **56**, 171; translated in Zeitsch. Phys. Chem., 1894, **15**, 106.

and of the Joule-Thomson coefficient presented in an earlier paper. In particular the choice of Knoblauch's values of C_p as the foundation of the determination of H in this paper is justified.

5. It is shown that Clausius' specific heat of saturated steam passes its maximum without becoming zero or positive, so that the temperature-entropy diagram for steam must be essentially simpler than that for either ether or chloroform.

6. The extrapolation formula for L mentioned in 3 above is made the basis of a determination of the critical density of water by the method of Cailletet and Mathias. The result is

$$v_c = 3.04 \text{ cm}^3/\text{gr}.$$

The specific volumes of water and of saturated steam at other high temperatures have also been computed and embodied in a steam table running up to the critical temperature.

JEFFERSON PHYSICAL LABORATORY,
CAMBRIDGE, MASS.,
December, 1909.